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CRYSTALLIZATION BEHAVIOR AND EFFECT OF THERMAL HISTORY ON FRACTURE PERFORMANCE OF GLASS FLAKE REINFORCED POLYPROPYLENE

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ABSTRACT

In this work, the role of interface and matrix morphology in fracture behavior of glass flake reinforced polypropylene was investigated. Differential scanning calorimetric analysis showed that silane coupling agent modified the crystallization behavior of the polypropylene matrix. The presence of dry blend silane treated glass flakes in polypropylene was found to induce the nucleation process and decrease the overall rate of crystallization. This effect was attributed to the physisorbed layer of silane on the glass flakes.

The effect of matrix morphology on the fracture performance was analyzed by post yield fracture mechanics on samples of different levels of crystallinity. An increase in matrix crystallinity in pure polypropylene and glass flakes polypropylene composites led to a reduction in the maximum crack growth resistance. The lower ductility of a more cystalline matrix resulted in a reduction of the energy dissipated in the matrix stretching and therefore, a concomitant decrease in the fracture energy.

Although the effect of matrix morphology seemed to be very important in the case of pure polypropylene and untreated glass flake polypropylene composites, this effect was found to be negligible for the silane treated composites. Nevertheless, microscopic observations of the fracture surfaces of silane treated composites also revealed a reduction in the ductility of the matrix in highly crystalline samples. An improvement in the matrix-filler interface seemed to inhibit the effect of matrix morphology on the fracture behavior of glass flake polypropylene composites.

INTRODUCTION

The development of glass-reinforced thermoplastic composites involves optimization of processing parameters, glass reinforcement content and reinforcement/matrix adhesion. Promoting adhesion at the filler/polymer interface permits the stress to be transferred from the polymer matrix to the reinforcement. In fact, a poorly bonded area at the interface will cause rupture of the interface at a very low stress (1). Coupling agent promotes adhesion and serves as the intermediate layer between the matrix and the reinforcement.

However, the effect of coupling agent on fracture performance of reinforced polypropylene is still unclear. While the modulus and strength increase (1,2), a reduction of the Izod fracture energy (3) and a decrease in the maximum crack growth resistance (4) were observed. The decrease in the fracture performance was attributed to the reduction of the matrix

ductility in the composite in the presence of coupling agent (5). The crack growth resistance of the composite was shown to be governed by a competition between voiding and stretching effects in the matrix (6-8). Voiding was formed under hydrostatic stress in the bulk region and drawing was promoted by shear plastic deformation around the filler boundary. A better interface could therefore increase the triaxiality of stress by reducing the matrix/filler debonding. Consequently, even though the debonding energy is increased by the use of coupling agent, the above effect can lead to a reduction in the fracture energy of the composite under certain conditions (5). Furthermore, previous work (9) has shown that the effect of coupling agent on the fracture behavior of glass flake reinforced polypropylene is dependent on filler concentration. While the addition of coupling agent had a detrimental effect at low concentration of filler, it showed a beneficial effect at high concentration. The fracture behavior of the untreated and silane treated glass flakes polypropylene composites are shown in Figure 1. This fracture behavior was qualitatively explained in terms of the competition between the contribution of the matrix/filler interface and that of the matrix to the fracture energy of the composites.

In addition to the adhesion effect, silane can alter the morphology of the matrix. This observation was previously reported by Chabert et al. (10) in γ-aminopropyl triethoxysilane treated glass fibers/polypropylene composites. Previous work (9) also showed that the addition of silane coupling agent in glass flake reinforced polypropylene

can modify the crystalline structure of the filler/matrix interface. This effect was found to be dependent on the method used to apply the coupling agent. Silane coupling agent, applied by the dry blend technique, induced specific nucleation at the filler surface, whereas the slurry treatment did not promote nucleation. This effect is shown in Figure 2.

In the case of a composite based on an unreactive resin such as polypropylene, a matrix/coupling agent interpenetrating network has been suggested (11,12) to be responsible for the improvement in filler/matrix adhesion. The interpenetrating network model states that the matrix and silane chains can diffuse into each other to form an entangled network in the interphase. This network could therefore have a significant effect on the crystallization process in the matrix. Furthermore, it is well known that the fracture performance of both pure polymer (13-15) and composite (15,17) may depend upon the matrix morphology.

The purpose of the present work is to investigate the crystallization behaviors and the effects of thermal history on the fracture performance of untreated and silane-treated-glass-flakes polypropylene composites.

EXPERIMENTAL

Materials

The polypropylene used in this study was an injection grade resin, Profax 6301, from Himont Canada Ltd. The resin was in powder form, and had a melt index of 12g/10 min (ASTM 1238). Glass flakes (Hammer-milled

Flake Glass 0.4 mm) were obtained from Owens Corning Fiber Glass, Toledo, OH.

Dow Corning Z-6032 silane, having the chemical formula $(CH_3O)_3$-Si-CH_2 $CH_2CH_2NHCH_2CH_2NHCH_2$-ϕ-CH=CH_2.HCl and designated as N-β-(N-vinylbenzyl-amino)ethyl-γ-aminopropyltrimethoxy silane monohydrogen chloride, was applied on the glass flakes by both a dry blend and a slurry technique. The dry blend treatment consisted of pulverizing a 10% solution of silane in methanol on the glass flakes while blending in an Attritor mixer. This process was done at approximately 60°C to evaporate the methanol. In order to simulate the degradation of the fillers during silane treatment, the uncoated fillers were also stirred in the mixer for the same duration. Using the slurry technique, the glass flakes were treated by immersion in a 2% aqueous solution of silane at a pH of 5. The slurry treated glass flakes were filtered on a Büchner filter and washed with distilled water. After the treatment, the glass flakes were briefly heated for approximately 15 minutes at 140°C in order to complete the condensation process.

Sample preparation

Polypropylene powders were dry blended with the glass flakes in a Welex high intensity mixer (Model ESK-80). The glass flake polypropylene samples were compression molded in a Carver press. To overcome the problem of air bubbles, the starting material for compression molding was a precompacted semi-crystalline plaque. The precompacted plaques were molded using a picture frame mold inserted between two aluminium plates.

Samples of different levels of crystallinity were obtained by cooling the molten plates at different cooling rates. The cooling time reported represents the time required to cool the melted sample from 200°C to 100°C assuming that the polypropylene crystalization under 100°C is negligible. For the fracture tests, three-point-bend specimens of 3 x 12 x 60 mm were cut out from compression molded plates. The initial cracks (a_o) were 4.8 mm long, giving a ratio of initial crack length to specimen width (a_o/D) of 0.4. A prenotch was first made by a saw cut and the final crack was created by forcing a razor blade into the specimen in a special jig on a laboratory press, giving a crack tip radius of less than 30 μm.

Differential scanning calorimetry (DSC) measurements

Differential scanning calorimetry measurements were done on a SETARAM Model CDP111 instrument using paired platinum crucibles. The sample of around 75 mg was cut out from the compression molded plate. The nonisothermal crystallization was carried out by holding the sample in the melt for 10 minutes at 220°C and then cooling at a constant rate of 5°C per minute. The operation was carried out under nitrogen atmosphere.

Microscopy

A scanning electron microscope (Type Jeol 35CF) was used to examine the fracture surfaces of the composites. An optical microscope (Leitz/Wetzlar, Dialux 20) was also used to obtain micrographs of polypropylene crystallization. In this case, the sample was held in the melt at 220°C for a period of 10 minutes. The crystallization was then observed at 120°C with crossed polarizers in the presence of a quartz filter.

Mechanical Testing

All tests were performed on a standard testing machine (Instron Model 1125). The critical stress intensity factor during crack propagation was calculated using the calibration factor $f(a_o/D)$ for the three-point-bend specimens provided in (18):

$$K_R = \frac{PS}{BD^{3/2}} \frac{a_{eff}}{D} \qquad (1)$$

where P is the load, S is the support span, B is the specimen thickness, D is the specimen width, and a_{eff} is the effective crack length which is the physical crack size augmented by the dimension of the plastic zone ahead of the crack tip. At each load level on the load-deflection diagram, the effective crack length (a_{eff}) was calculated from the instantaneous compliance, C, determined by the secant passing through the origin of the load-deflection curve as discussed in (19). The calculated critical stress intensity factor, which represents the crack growth resistance of the material, was then plotted as a function of effective crack growth $\Delta a_{eff}(a_{eff} - a_o)$. For all the mechanical tests, an average value was determined from at least six samples.

RESULTS AND DISCUSSIONS

Crystallization behavior

The optical microscopic observation in the previous work (9), has shown that the addition of silane coupling agent in glass flake

polypropylene composites can modify the morphology of the polypropylene matrix at the interface. This effect was found to depend on the method used to apply the silane on glass flakes (Figure 2). The crystallization analysis of the same system by differential scanning calorimetry (DSC) concurs with the optical microscopic observations. Figure 3 shows the crystallization exotherms of the untreated and dry-blend-treated glass-flake polypropylene composites of different filler contents. The crystallization exotherm of the slurry treated 30 wt% glass flake composite is also reported in Figure 3.

Table 1 summarizes the information obtained from the DSC thermograms. The following parameters are reported:

- The onset temperature of crystallization, T_{onset}, which is the temperature where the thermogram initially departs from the base line.

- The temperature where the exotherm peak shows a maximum, denoted as T_p.

- The area under the exotherm peak divided by the mass of the polypropylene in the composite, A/m. Since measurements for all samples were made with identical settings of the instrument, A/m is hence proportional to the heat of crystallization of the given sample and thus to its degree of crystallinity.

- The half time of crystallization, $t_{\frac{1}{2}}$.

As observed by optical microscopy, DSC analysis shows that untreated glass flakes and glass flakes treated by the slurry treatment do not act as nucleating agents for polypropylene while the dry blend treated glass flakes significantly increase the onset temperature of crystallization indicating the nucleating ability of these fillers. Moreover, as suspected, increasing the fraction of dry blend silane treated glass flakes in polypropylene produces a shift of the onset of crystallization toward higher temperatures. An increase in the fraction of untreated glass flakes in polypropylene does not affect this parameter.

A study of the non-isothermal rate of crystallization of the untreated and the silane treated composites is shown in Figure 4. Assuming that the crystallization enthalpy is directly related to the crystallized polymer, the transformed fraction of polypropylene is obtained by the integration of the crystallization exotherm. Three domains have been considered for the curve of the transformed fraction of polypropylene as a function of time (20): domain I represents the transformed fraction involved between 0 and 0.2, domain II corresponds to the transformed fraction between 0.2 and 0.8 and domain III, involving the transformed fraction of 0.8 to 1, corresponds to the end of the crystallization.

In domain I, corresponding to the beginning of crystallization, it can be observed that the addition of untreated glass flakes in polypropylene seems to increase the rate of transformation whereas the dry blend silane treated glass flakes produce a decrease in the rate of transformation above 30 wt%. To obtain a transformed fraction of 0.2 it takes 110 seconds for the pure polypropylene, 80 seconds for the polypropylene filled with 50% of untreated glass flakes and 134 seconds for the polypropylene filled with 50% of silane treated glass flakes. At 30%, glass flakes treated with silane using the slurry technique seem to produce almost the same effect as the untreated glass flakes. A transformed fraction of 0.2 is obtained in 90 seconds for the untreated and the slurry treated glass flake composite while 118 seconds are required for the dry blend treated composite of the same composition.

In domain II, all of the crystallization curves are parallel. The position of these curves on the time scale results from the time shift induced in domain I.

In domain III, it can be seen that the presence of glass flakes, with and without treatment, decreases the rate of transformation of the polypropylene. In fact, to increase the transformed fraction from 0.8 to 1, it takes 36 seconds for pure polypropylene, 51 seconds for polypropylene filled with 50% of untreated glass flakes and 59 seconds for polypropylene filled with 50% of silane treated glass flakes.

It is well known that two phenomena are involved in the first stage of the crystallization process: the nucleation and the beginning of the development of these crystalline entities. Optical microscopy (Figure 2) has shown that dry blend silane treated glass flakes are better nucleating agents than untreated and slurry treated glass flakes. Silane coupling agent, when applied by the dry blend technique, was found to increase the nucleation density during the crystallization of polypropylene. Consequently, the decrease of the rate of transformation of polypropylene observed in the presence of dry blend silane treated glass flakes can be associated with the low rate of development of the crystalline entities.

This result could possibly be explained by the fact that in the presence of dry blend silane treated glass flakes, the crystallization begins at the glass flake surface where the development of the crystalline entities is hindered in space due to the presence of the glass flakes. A similar mode of crystallization was observed in the case of polymer crystallized in the presence of carbon (21-23) or Kevlar fibers (24) where transcrystalline structure occurs. In such a case, the growth of the crystalline entities is not in three dimensions but rather in two. Consequently, in the first stage of crystallization, the rate of transformation in the case of dry blend silane treated composite is lowered. Moreover, at a later stage, the spherulitic crystallization in the bulk polypropylene commences. This results in a crystallization rate similar to the case of untreated composites.

In the third domain of crystallization, it can be observed that both untreated and silane treated glass flake composites have a lower rate of transformation than pure polypropylene. This result can be associated with the truncation effect observed in the final stage of development of the crystalline entities. The high nucleation density and the presence of the glass flakes should be responsible for this disturbance. A similar result was already reported for the system of glass fiber/polyamide, 6-6 (20).

The constant value of A/m obtained for all of the samples indicates that while dry blend treatment decreases the overall rate of crystallization of the composite it does not affect the total level of crystallinity of the polypropylene matrix. This result is not in contradiction with the interpenetrating network concept (11,12) where the polymer matrix has only a physical interaction with the silane layer.

In summary, from the DSC analysis, it was observed that silane coupling agent applied by the dry blend technique produces a significant decrease of the overall rate of crystallization of the glass flake polypropylene composites and this effect was found to be dominant in the first stage of crystallization which involves the development of the crystalline entities at the glass/polypropylene interface. Moreover, as suspected, the effect of coupling agent on the overall rate of crystallization is more important in the case of composites of higher filler content where the interfacial contribution becomes dominant.

Effect of thermal history on fracture performance

In the first step, the effect of thermal history on fracture performance was investigated for pure polypropylene. Figure 5 shows micrographs of microtomed films of compression molded plates obtained from different cooling rates. It can be seen that the quenched sample (Figure 5a) displays a morphology in which the spherulitic structure of polypropylene is absent whereas the sample obtained after a long cooling time shows well-defined spherulites (Figure 5c). Due to low heating rate of the DSC analyser the relative level of crystallinity of the polypropylene sample was evaluated by density measurements. Figure 6 shows the variation of polypropylene density as a function of thermal treatment. Considering the density of amorphous PP to be 0.855 and that of pure crystalline PP to be 0.936 (25), the degree of crystallinity varies in the range of 55 to 65% with increasing spherulite diameter for the above thermal treatment. The value of 65% obtained for the high crystalline sample is in accordance with the degree of crystallinity obtained from the analysis of the exotherm of the DSC measurements (Table 1).

The fracture toughness tests on three-point-bend specimens showed that a change in polypropylene morphology significantly affects the fracture performance but does not modify the mode of fracture. The fracture remains unstable in all cases. Figure 7 shows the maximum crack growth resistance, K_{Rmax}, of polypropylene having different levels of crystallinity. As can be expected, a higher fracture performance was obtained for samples of lower crystallinity and hence for the finest

spherulitic structure. In fact, in this type of morphology, a dense craze formation in front of the crack tip provides high energy dissipation (15).

Using the same procedure as that of the pure polypropylene, the effect of matrix morphology on the fracture behavior of untreated and silane treated glass flakes polypropylene was investigated. Figure 8 shows the K_{Rmax} of the untreated and the silane treated 30% glass flake composites obtained from different thermal histories. For comparison, the results obtained for the pure polypropylene processed under the same conditions are also reported. As observed for the pure polypropylene, an increase in crystallinity in untreated glass flake polypropylene composite results in a strong decrease in the crack growth resistance of the composites. Surprisingly enough, the fracture performance of the silane treated composite is only slightly affected by thermal history. This occurs in spite of the fact that the density measurements showed the same variation for the untreated and silane treated composites. Density measurements of pure polypropylene, untreated and silane treated glass flakes polypropylene composites obtained from different thermal treatments are presented in Table II. Figure 9 shows the fracture surface of these composites obtained from a cooling time of 15 seconds and from an annealing period of five days. The higher crystalline structure of the annealed samples results in a lower ductility of the matrix.

The decrease of K_{Rmax} observed for the untreated glass flake polypropylene composites as a function of cooling time is consistent with

the reduction in matrix ductility of a highly crystalline structure. As suspected, the microscopic plastic deformation of the highly crystalline composite is less pronounced than that of a composite having a lower crystallinity. Moreover, the reduction in K_{Rmax} as a function of thermal history for the untreated composites and the pure polypropylene is the same. Previous work (6) on the microductility of mica and glass flake filled polypropylene has shown that the crack propagation resistance of the composite is mainly due to plastic deformation of the matrix, aided by the debonding between reinforcements and polypropylene. However, the debonding process is not dependent on the morphological state and hence the decrease in the maximum crack growth resistance observed by increasing the level of crystallinity of the composite is due only to a reduction of ductility of the matrix. This results in the same reduction of crack growth resistance in pure polypropylene and untreated composite.

Figure 8 shows that the fracture behavior of the silane treated composite is quite different in comparison to that of the untreated composite. In fact, thermal history has an almost negligible effect on the fracture performance in spite of the fact that the fracture surfaces (Figure 9) of the highly crystalline matrix samples show a lower ductility compared to the low crystallinity samples.

As shown in the previous work (9), the fracture behavior of the composite could be explained in terms of contributions of filler/matrix interface and plastic deformation of the matrix. While the contribution

of the matrix is strongly dependent on thermal history, the adhesion process could be independent of morphological change. Consequently, the above result could possibly be explained by a dominant role of the interface at this filler concentration.

Figure 11 and 12 show the effect of thermal history on the fracture behavior of silane treated and untreated glass flake polypropylene composites of different compositions. Figure 11 demonstrates that the effect of matrix crystallinity is reduced as the filler content increases in untreated composites. However, in the case of treated glass-flakes, regardless of filler content, matrix crystallinity has almost no effect on the crack growth resistance of the composite.

This result is rather surprising since at low filler content the interface contribution could be expected to be negligible and a variation in matrix crystallinity would result in a change in fracture performance. It is not clear for the moment why the presence of silane seems to inhibit the effect of morphological change on fracture resistance of the composite. Further evidence for this observation can be found in comparing the crack growth resistance of samples in which glass flakes are treated by slurry and dry blend techniques, since it has been shown above that the method of treatment can alter the matrix morpholgy. Figure 13 shows the variation of the crack growth resistance as a function of crack extension for the case of silane treated glass flakes prepared by the slurry and by the dry blend techniques. These curves show that regardless

of the observed change in matrix morphology, the method of silane treatment does not affect the fracture performance of the composite.

SUMMARY AND CONCLUSION

The presence of silane coupling agent in glass flake polypropylene composite was found to modify the morphology and the crystallization behavior of the polypropylene matrix and this effect depends on the method used to apply silane. When the coupling agent is applied by the dry blend technique, it was found to induce nucleation at filler-matrix interface and to decrease the overall rate of crystallization of the composite. The decrease of the overall rate of crystallization observed in the first stage of the crystallization process was attributed to the low development of the crystalline entities present on the dry blend silane treated glass flakes. Crystallization at glass flake surface seems to adopt a pseudo-transcrystalline structure where the growth of the crystalline entities is hindered in space due to the presence of the glass flakes. When silane is applied by slurry treatment, the crystallization behavior of the treated composite was found to be similar to the untreated composite due to the low nucleating ability of the slurry treated glass flakes. Moreover, at a later stage of crystallization, the interfacial effect decreases and the crystallization behavior of the dry blend silane treated composite was found to be similar to the slurry and the untreated glass flake composites. At the final stage of crystallization, both the untreated and silane treated composites were found to have a lower rate of transformation than pure polypropylene.

Truncation effect due to high nucleation density and glass flakes themselves are probably responsible for this result.

Thermal history was found to affect the fracture behavior of pure polypropylene and untreated glass flake polypropylene composite. An increase in the matrix crystallinity significantly decreases the maximum crack growth resistance. This reduction is consistent with the reduction in ductility of a highly crystalline matrix. In addition, the reduction of K_{Rmax} observed for the pure polypropylene and the untreated glass flake polypropylene composite was found to be of the same order of magnitude suggesting that the fracture behavior of the untreated composite is dominated by the matrix morphology. Moreover, the fracture performance of the dry blend silane treated composite was found to be only slightly affected by the matrix morphology regardless of filler content. This behavior is rather surprising since at low filler content the interfacial contribution is not significant in comparison to that of the bulk matrix. Further work is needed to clarify this effect of silane coupling agent.

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FIGURE CAPTIONS

Figure 1 - Maximum crack growth resistance as a function of filler concentration for the untreated and the silane treated glass-flakes reinforced polypropylene.

Figure 2 - Micrographs of the onset of crystallization of polypropylene in presence of: (a) untreated glass-flakes, (b) dry-blend silane treated glass-flakes and (c) solution treated glass-flakes.

Figure 3 - Crystallization exotherms of the untreated and the dry-blend treated glass-flake polypropylene composites of different filler contents. The crystallization exotherm of the pure polypropylene and the slurry treated 30% wt% glass-flake composite are also reported.

Figure 4 - Transformed fraction of polypropylene as a function of time for untreated and silane treated glass-flakes polypropylene composite.

Figure 5 - Micrographs of microtomed film of compression molded plates of polypropylene obtained from different cooling rates: (a) cooled in 15 seconds, (b) cooled in 2 minutes and (c) cooled in 4 minutes.

Figure 6 - Variation of polypropylene density as a function of the thermal treatment.

Figure 7 - Variation of the maximum crack growth resistance, K_{Rmax}, for pure polypropylene of different levels of crystallinity.

Figure 8 - Maximum crack growth resistance of pure polypropylene, untreated and silane treated 30% glass-flake polypropylene composites obtained from different thermal treatment.

Figure 9 - Micrographs of fracture surface of untreated and silane treated 30% glass-flake polypropylene composites obtained from a cooling time of 15 seconds and from an annealing period of five days.

Figure 10 - Maximum crack growth resistance of untreated glass-flake polypropylene composites obtained from two different thermal histories; quenched and annealed.

Figure 11 - Maximum crack growth resistance of dry-blend silane treated glass-flakes polypropylene composites obtained from two different thermal histories; quenched and annealed.

TABLE CAPTIONS

Table I - Data obtained from the DSC analysis.

Table II - Density measurements of pure polypropylene untreated and silane treated glass flake polypropylene composite in the quenched and annealed forms.

TABLE I - Data obtained from the DSC analysis

Samples	T_{onset}	T_p	$t_{\frac{1}{2}}$ (min)	A/m j/g	% C
PP	129	116	2.76	94.06	65
PP/P.1	130	117	2.54	98.05	68
PP/P.3	130	118.5	2.36	97.03	67
PP/P.5	130	121	1.96	97.05	67
PP/P.1/Si	131	119	2.38	95.84	66
PP/P.3/Si	135	122.5	2.62	97.72	68
PP/P.5/Si	138	124	2.96	96.10	67
PP/P.3/Si Solution	130.5	119.5	2.33	97.10	67

TABLE II - Density measurements of pure polvp pylene untreated and silane treated glass flake polypropylene composite in the quenched and annealed forms.

SAMPLE	DENSITY	
	QUENCHED	ANNEALED
PP	0.9026	0.9080
PP/P.1	0.9444	0.9654
PP/P.1/Si	0.9440	0.9654
PP/P.3	1.1103	1.1215
PP/P.3/Si	1.1187	1.1306
PP/P.5	1.3250	1.3330
PP/P.5/Si	1.3245	1.3327

شکل ۱

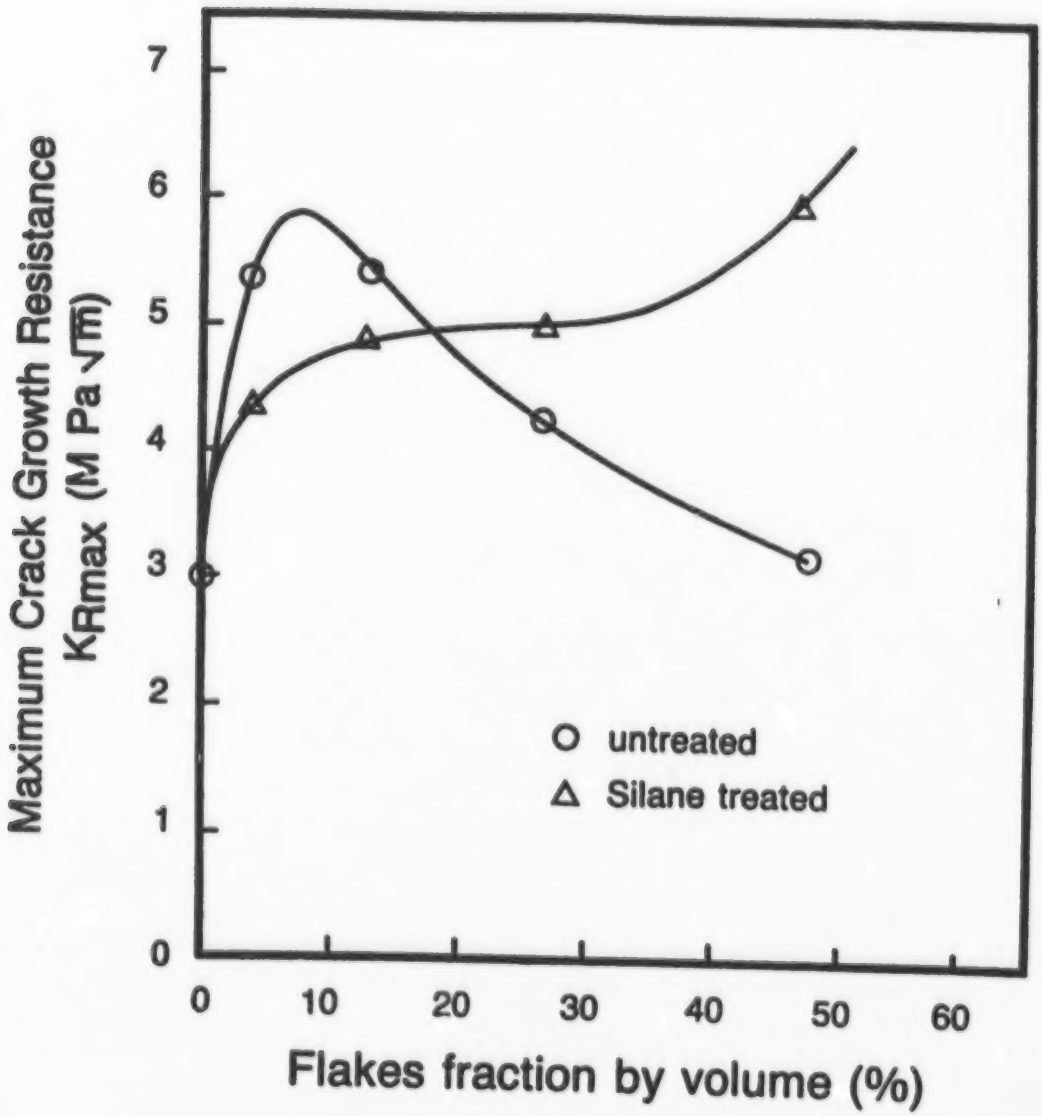
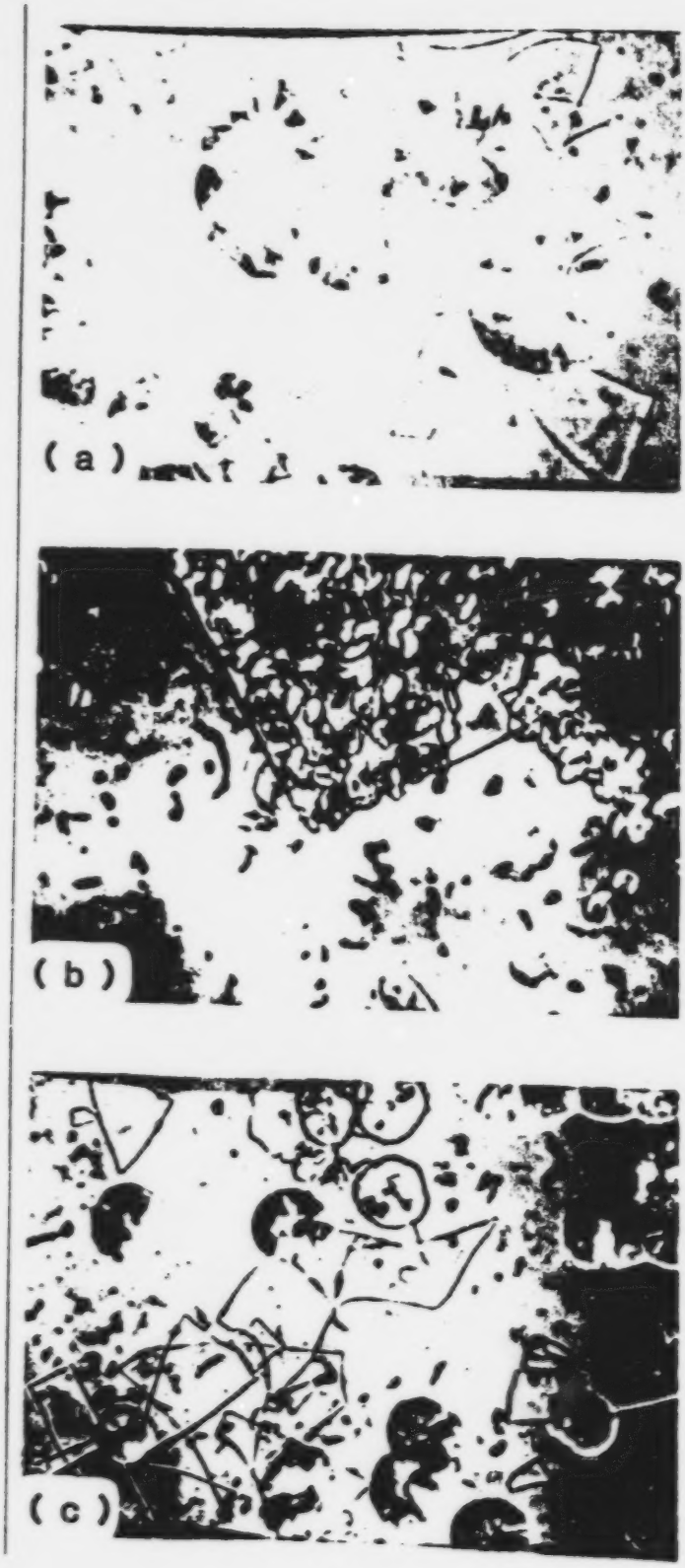

Maximum Crack Growth Resistance
K_{Rmax} (M Pa $\sqrt{m}$)
7
6
5
4
3
2
1
0
0
10
20
30
40
50
60
Flakes fraction by volume (%)
untreated
Silane treated

Fig. 2



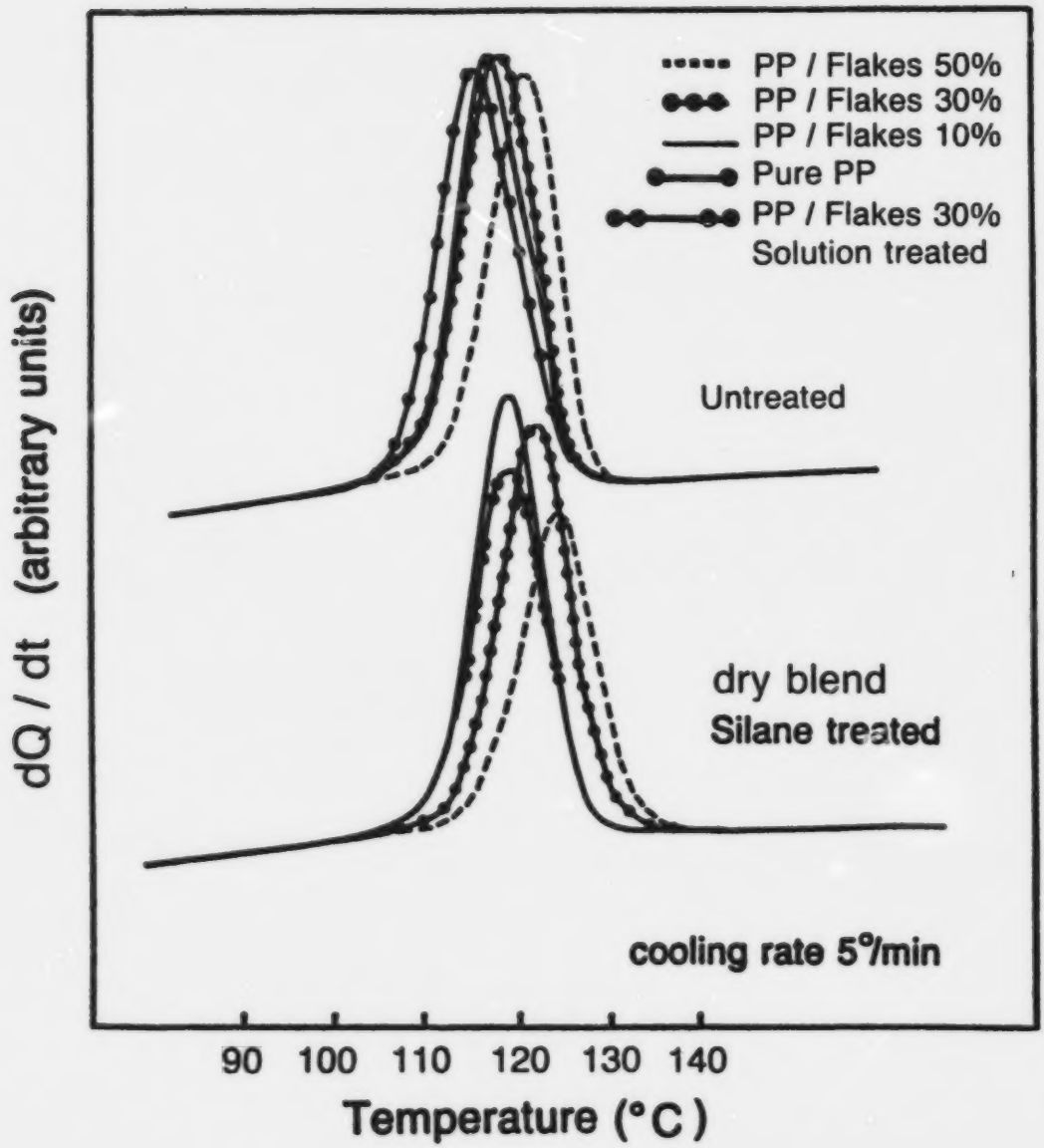

PP / Flakes 50%
PP / Flakes 30%
PP / Flakes 10%
Pure PP
PP / Flakes 30%
Solution treated
Untreated
dry blend
Silane treated
cooling rate 5°/min
dQ / dt (arbitrary units)
90 100 110 120 130 140
Temperature (°C)

Fig. 4

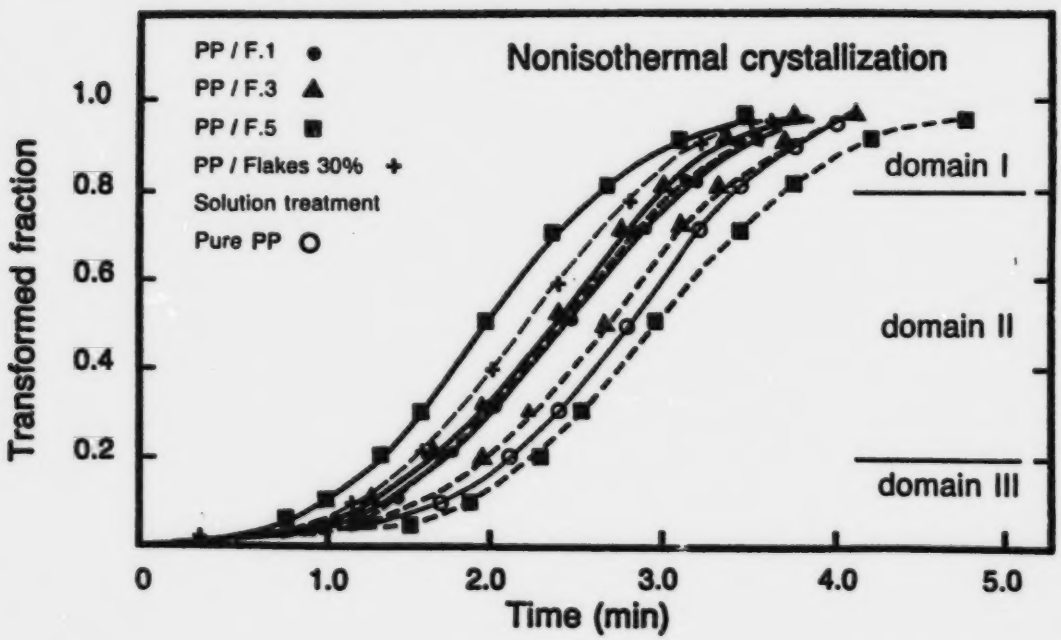
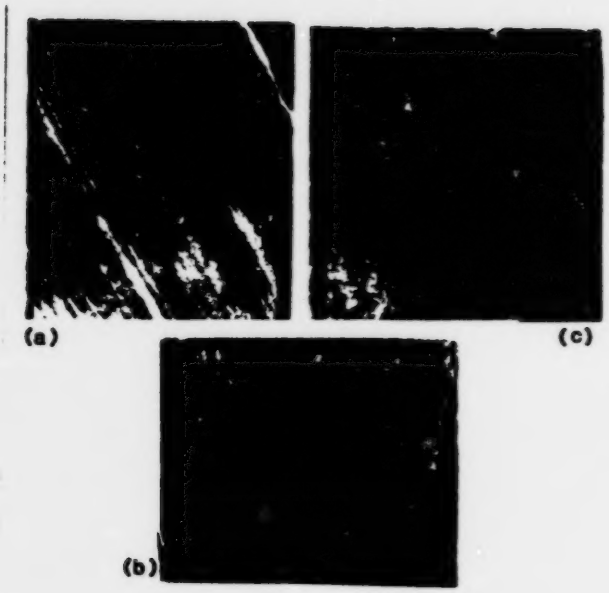

Nonisothermal crystallization
PP / F.1
PP / F.3
PP / F.5
PP / Flakes 30%
Solution treatment
Pure PP
domain I
domain II
domain III
Transformed fraction
1.0
0.8
0.6
0.4
0.2
0
1.0
2.0
3.0
4.0
5.0
Time (min)

Fig. 5



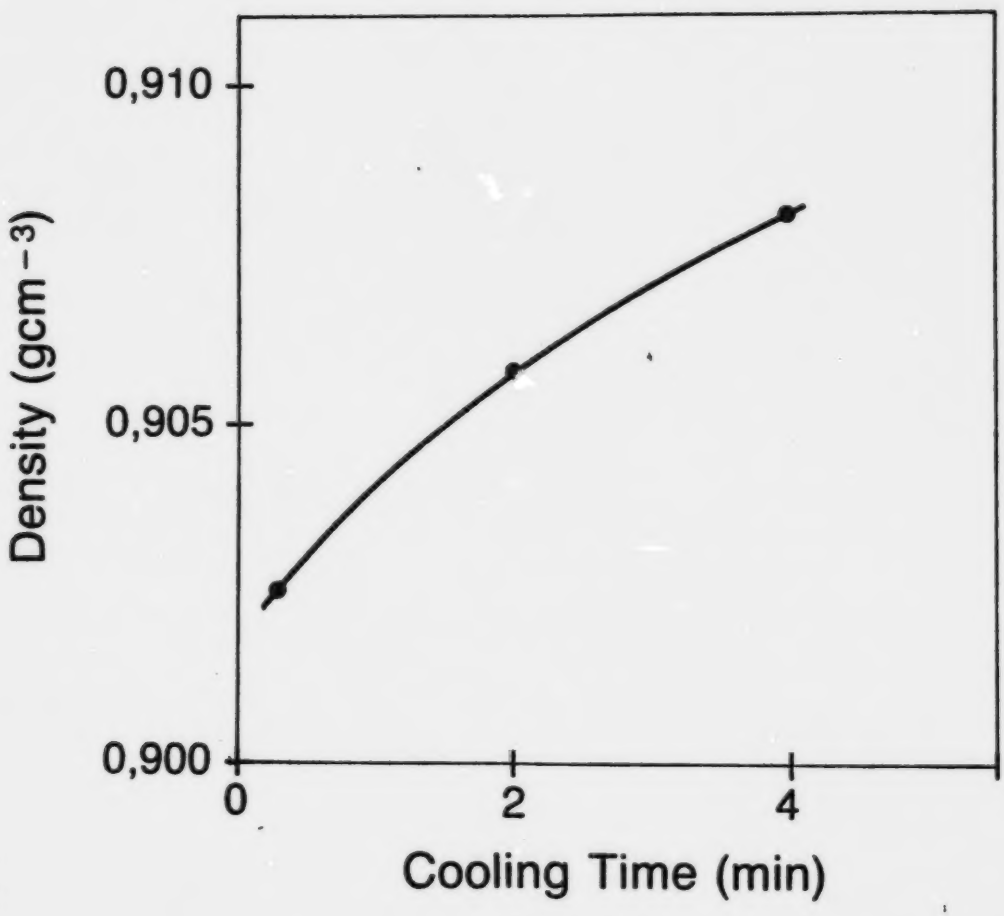
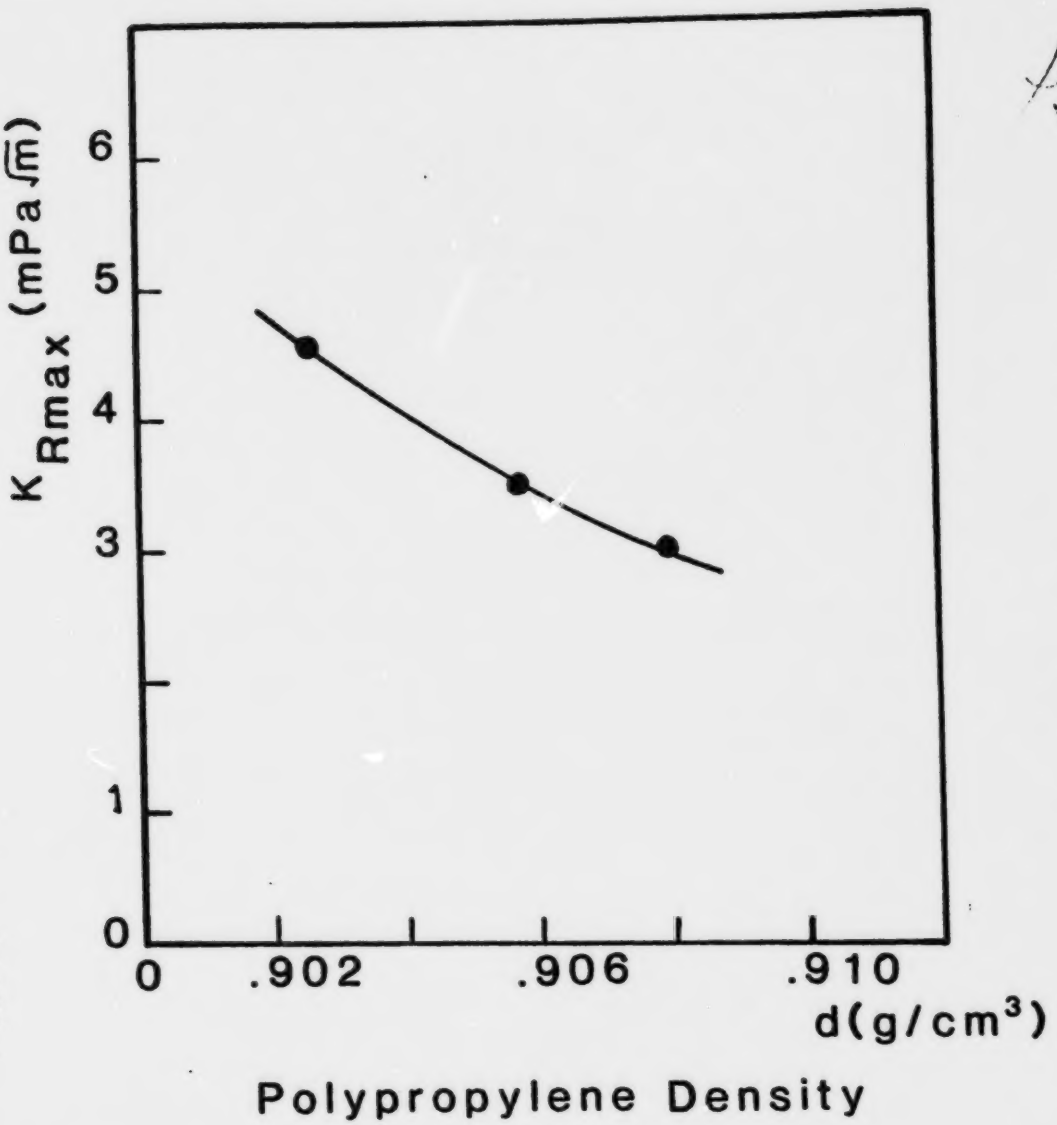


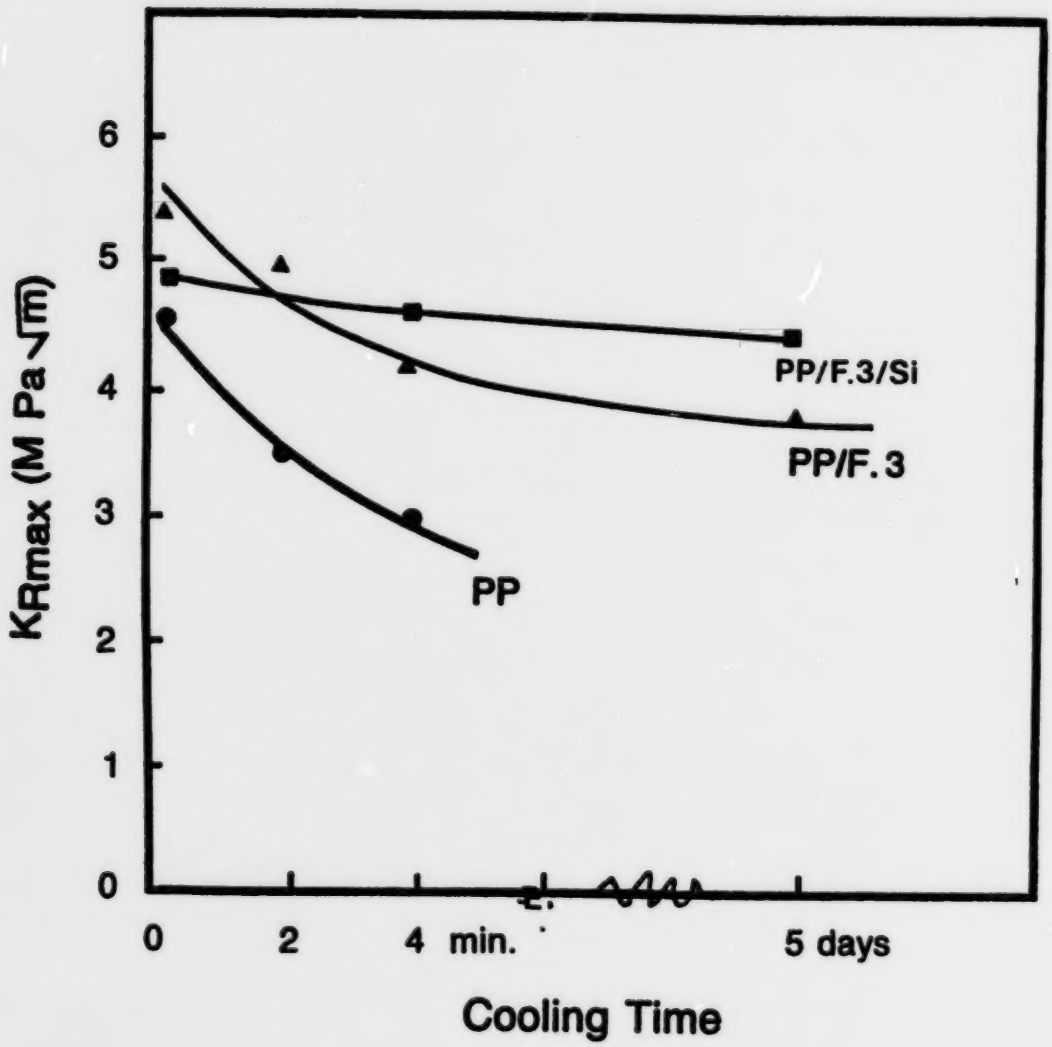
fig. 6

Fig. 1

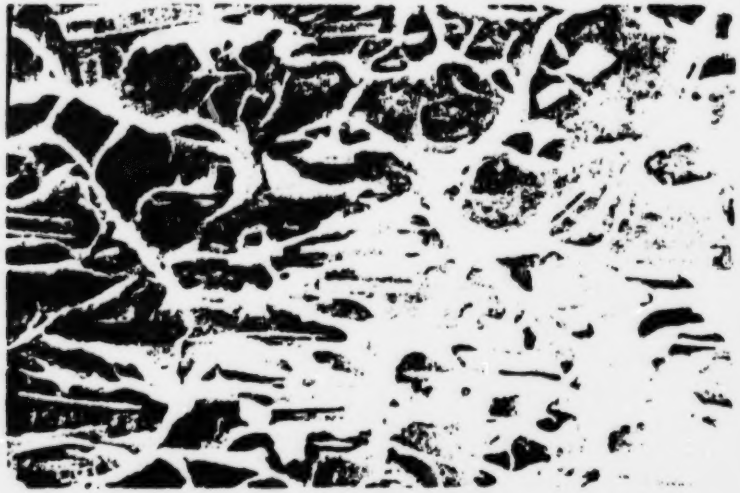


Polypropylene Density

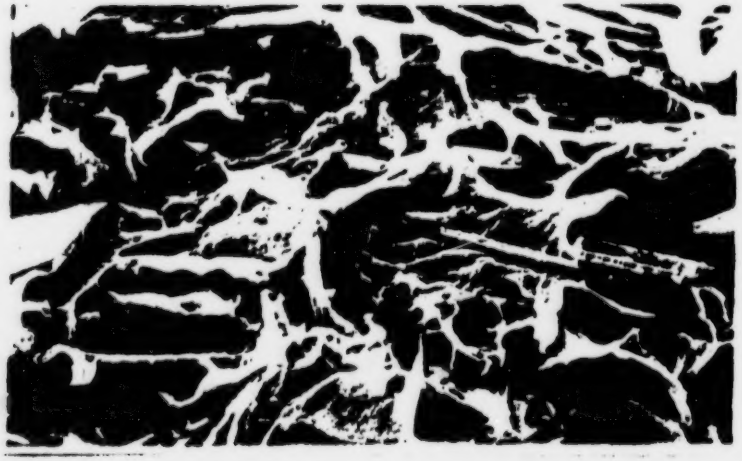
Fig. 9


6
5
4
3
2
1
0
KRmax (M Pa√m)
PP/F.3/Si
PP/F.3
PP
0
2
4 min.
5 days
Cooling Time

QUENCHED



ANNEALED



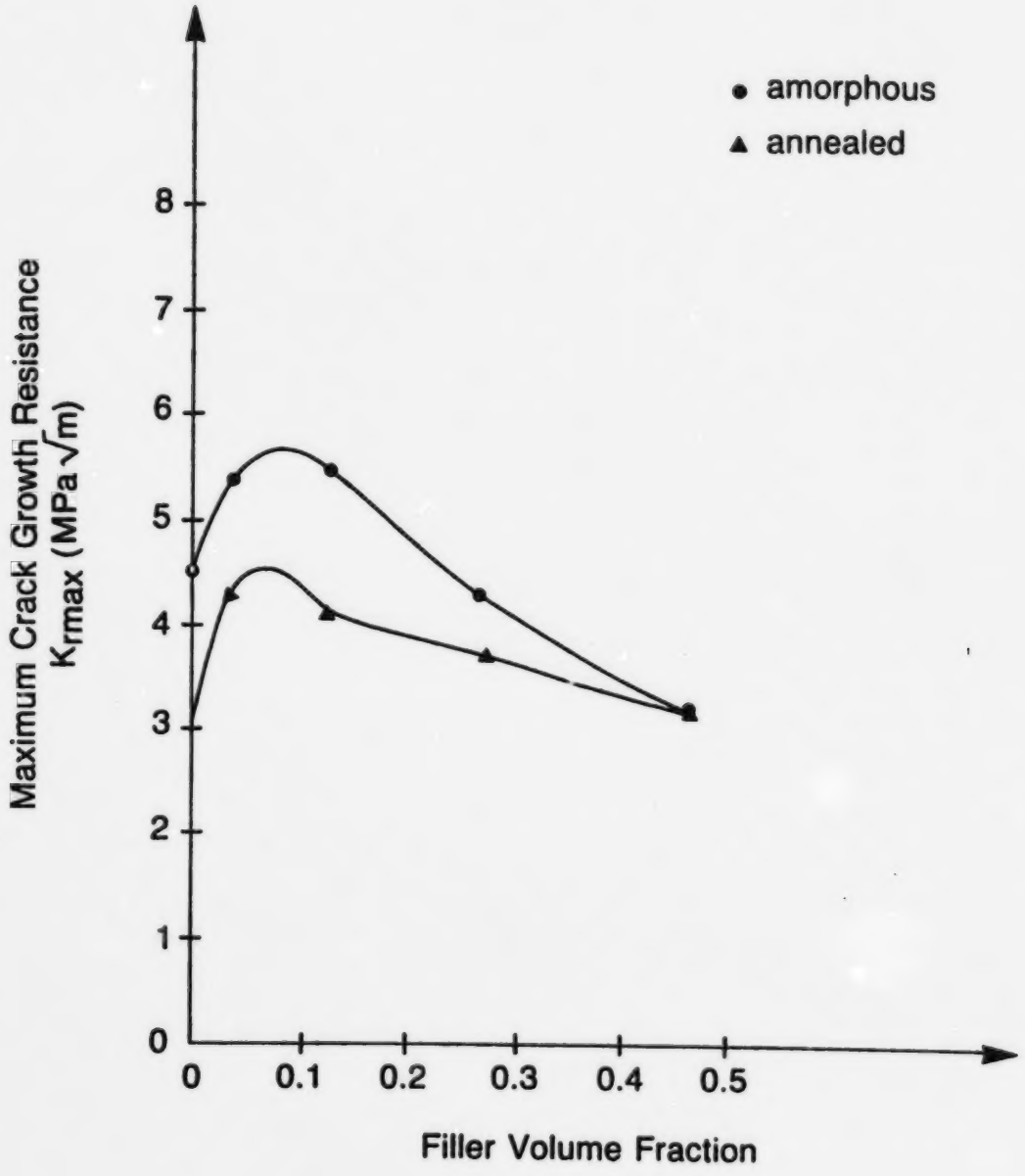

amorphous
annealed
Maximum Crack Growth Resistance
K_{rmax} (MPa $\sqrt{m}$)
0
1
2
3
4
5
6
7
8
0
0.1
0.2
0.3
0.4
0.5
Filler Volume Fraction

Fig. 12

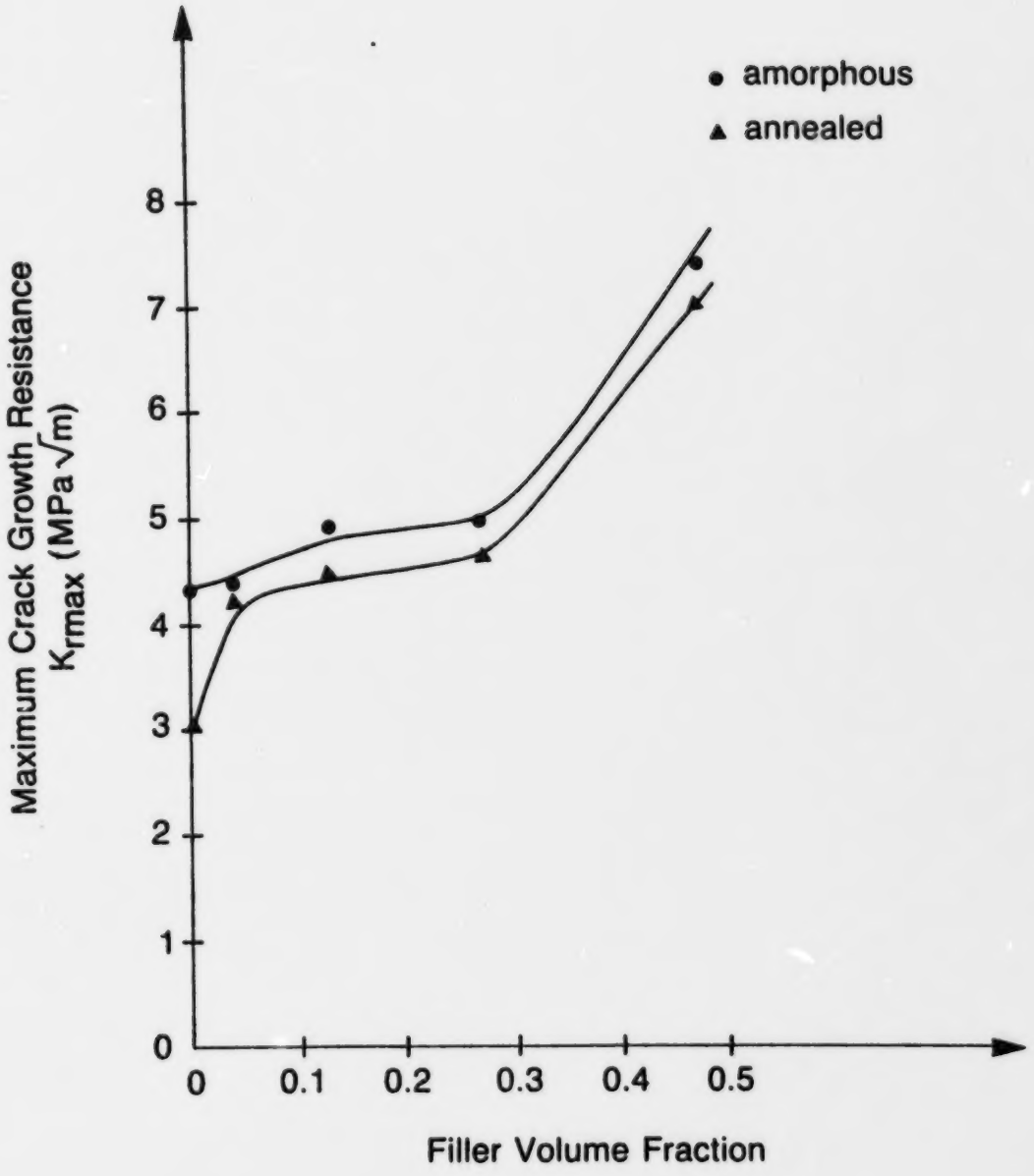

amorphous
annealed
Maximum Crack Growth Resistance
K_{rmax} (MPa $\sqrt{m}$)
8
7
6
5
4
3
2
1
0
0
0.1
0.2
0.3
0.4
0.5
Filler Volume Fraction

Fig. 11